Wetting phenomena in bcc binary alloys¹

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Abstract

The wetting behavior at the free (100) surface of a bcc binary alloy exhibiting a continuous order-disorder transition in the bulk is investigated theoretically, using a model equivalent to a bcc Ising antiferromagnet in an external magnetic field. Its salient feature is the generation of an effective ordering surface field, $g_1 \neq 0$, for certain symmetry-breaking surface orientations like (100). Such a field, coupling to the local order parameter at the surface, does not only crucially affect the surface critical behavior at bulk criticality, but also leads to the occurrence of wetting phenomena below the critical temperature T_c . Starting from the mean-field theory for the lattice model and making a continuum approximation, a suitable Ginzburg-Landau model is derived. Explicit results for the dependence of its parameters (e.g., of g_1) on the microscopic interaction constants are obtained. Utilizing these in conjunction with Landau theory, the wetting phase diagram is calculated.

KEY WORDS: antiphase boundary, bcc binary alloys, complete wetting, Landau-Ginzburg models, noncritical densities, surface critical behavior

1 Introduction

Surface critical behavior at bulk critical points can be divided into distinct universality classes [1]. For a given bulk universality class, only gross surface properties determine which surface universality class applies, such as: whether or not the surface interactions exceed or are equal to a certain critical enhancement, or whether a surface field g_1 coupling to the local order parameter exists. Recently it has been shown that the universal critical behavior at the surface of a bcc Ising antiferromagnet and of a binary alloy undergoing a continuous order-disorder bulk transition depends crucially on the orientation of the surface with respect to the crystal axes [2, 3]. The basic mechanism underlying this intriguing behavior is the interplay between broken translational invariance perpendicular to the surface and the symmetry with respect to *sublattice ordering*. For certain "symmetry-breaking" orientations an "effective" ordering surface field $g_1 \neq 0$ emerges, which depends on physical parameters like temperature and bulk composition of the alloy. That such a field exists has already been pointed out in [4] in order to explain the persistence of surface order at a (100) surface above the bulk critical temperature T_c , detected in a Monte Carlo simulation for the A2–B2 order-disorder transition in Fe–Al.

The situation encountered for symmetry-breaking surfaces closely resembles the critical adsorption of fluids, where generically $g_1 \neq 0$ [5]. However, in that case the microscopic origin of g_1 is quite different: It is an external field reflecting, e. g., the preference of the wall for one of the two components of the binary liquid mixture. The transition that takes place at the surface of the system in the presence of a field $g_1 \neq 0$ on approaching the bulk critical point has been called normal in [6]. If $g_1 = 0$ (and the surface interactions are not too strongly enhanced), another transition, called ordinary, occurs. In accordance with the fact that g_1 is a relevant scaling field, the ordinary and normal transitions represent different surface universality classes.

In Refs. [2] and [3] the focus has been on the behavior at $T = T_c$ and a clear identification of the normal transition, which may also be regarded as a critical point wetting phenomenon [7]. However, since g_1 generally stays nonzero away from T_c for symmetry-breaking surfaces, a variety of wetting phenomena may occur for $T < T_c$. Below we will determine the wetting phase diagram for a (100) surface within the mean-field approximation, utilizing the continuum model derived in [3]. Our work complements previous studies on wetting in fcc Ising antiferromagnets or binary alloys [8] as well as on interface roughening at an antiphase boundary in the [100] direction in bcc binary alloys [9].

The organization of the paper is as follows. In the next section we define our model, explain the difference between symmetry-breaking and symmetry-preserving surfaces, and then briefly discuss the discrete mean-field equations (Sec. 2). In Sec. 3 we introduce the Landau-Ginzburg model for the (100) surface derived in [3]. This is then used in Sec. 4 to determine the wetting phase diagram.

2 Lattice model

2.1 Definition

To model the continuous A2–B2 order-disorder transition in the binary (AB) alloys FeAl or FeCo, we consider a bcc Ising antiferromagnet with nearest-neighbor (NN) interactions of strength J < 0. The spin variable σ_i takes the values +1 or -1 depending on whether lattice site i is occupied by an A or B atom. Within the grand-canonical ensemble, the Ising Hamiltonian reads:

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i - H_1 \sum_{i \in \text{surf}} \sigma_i , \qquad (1)$$

where $\sum_{\langle i,j\rangle}$ runs over all NN bonds. The bulk field H serves to adjust the composition of the alloy and represents the chemical potential difference between A and B atoms. A nonzero surface field H_1 occurs generically in binary alloys, giving rise

to surface segregation effects. One has $H_1 > 0$ ($H_1 < 0$) if A (B) atoms tend to segregate at the surface. It is important not to confuse H_1 with an "ordering" field, which couples directly to the local order parameter. Only if H_1 distinguishes one of the two sublattices at the surface, as is the case for symmetry-breaking surface orientations where the surface sites belong to a single sublattice only (see below), will H_1 contribute to an "effective" ordering field g_1 . But even then $H_1 \neq 0$ is not a necessary condition for $g_1 \neq 0$ (cf. Sec. 3).

The average concentration (or occupation probability) c_i of A atoms on lattice site i can be written in terms of the mean magnetization $m_i \equiv \langle \sigma_i \rangle$ of spin σ_i as $c_i = \frac{1}{2}(1+m_i)$. In the ordered (B2) phase, the bcc lattice splits into two interpenetrating sc sublattices α and β with bulk magnetizations $m_b^{\alpha} \neq m_b^{\beta}$, which are preferentially occupied by A and B atoms, respectively (cf. Fig. 1). The disordered (A2) structure is characterized by $m_b^{\alpha} = m_b^{\beta} =: m_{\text{dis}}$. The bulk order parameter is defined by

$$\phi_b \equiv \frac{1}{2} \left(m_b^{\alpha} - m_b^{\beta} \right) \,. \tag{2}$$

2.2 Symmetry properties of the surface

Let us define more precisely what is meant by symmetry-breaking and symmetry-preserving surfaces. Consider a uniform translation $\tau_{\alpha\beta}$ of the crystal lattice that maps α -sites into β -sites. In an infinite system without free surfaces or a finite system with periodic boundary conditions, the Hamiltonian $\mathcal{H} = \mathcal{H}\{\sigma_i\}$, Eq. (1), is *invariant* under the transformation:

$$\sigma_i \to \sigma_i' = \sigma_{i+\tau_{\alpha\beta}} \,.$$
 (3)

This symmetry is spontaneously broken below T_c where the mean magnetizations m_b^{α} and m_b^{β} transform into each other under (3), so that $\phi_b \to -\phi_b$. For a system with a free surface, the invariance of the Hamiltonian still holds if $\tau_{\alpha\beta}$ can be taken parallel to the surface as is the case for the (110) orientation (Fig. 1). Then the

surface is called symmetry-preserving. One may convince oneself that a surface with Miller indices $(n_1n_2n_3)$ is symmetry-preserving if and only if $n_1+n_2+n_3$ is even. (By convention, we use the cubic unit cell of the bcc lattice here.) The order parameter, which becomes a local quantity $\phi = \phi_n$ depending on the discrete layer index n, vanishes identically above T_c since the $\phi \to -\phi$ symmetry of the bulk system is retained and no enhanced surface interactions have been admitted in (1). By contrast, if either one of the lattice planes parallel to the surface belongs to a single sublattice, as is the case for the (100) surface (Fig. 1), no translation $\tau_{\alpha\beta}$ parallel to the surface exists and the surface is called symmetry-breaking. Generally, a $(n_1n_2n_3)$ surface is symmetry-breaking if $n_1 + n_2 + n_3$ is odd. Then the Hamiltonian is no longer invariant under (3) but changes by an amount proportional to the total number of surface sites. (One may again consider a finite system but impose periodic boundary conditions only in the directions parallel to the surface.) Thus the $\phi \to -\phi$ symmetry of the bulk system is generically broken, and the order parameter will be nonvanishing at least locally near the surface even if $T \geq T_c$.

The symmetry properties of the surface must also show up in the context of suitable continuum (Landau-Ginzburg) models. Let ϕ_s be the value of the order parameter at the surface. For symmetry-preserving surfaces, the surface contribution to the Landau free energy will only contain *even* powers of ϕ_s . By contrast, arbitrary *odd* powers are expected to occur for symmetry-breaking surfaces due to the loss of the $\phi \to -\phi$ symmetry. In particular, the coefficient of the linear term may be identified with an "effective" ordering surface field $g_1 \neq 0$. Of course, in order to estimate the magnitude of g_1 and its dependence on physical parameters such as temperature and bulk composition, the parameters of the continuum model must be related explicitly to lattice quantities (see Sec. 3).

2.3 Mean-field (Bragg-Williams) approximation

Owing to the spatial inhomogeneity along the z axis perpendicular to the surface, exact treatments of the model (1) are very hard, and one usually has to rely on approximate techniques such as the mean-field (MF) or Bragg-Williams approximation. The MF equations read (with k_B = Boltzmann's constant):

$$m_i = \tanh\left[\frac{1}{k_B T} \left(H_i - J \sum_j^{(i)} m_j\right)\right], \qquad (4)$$

where $H_i = H$, $H_i = H + H_1$ for bulk and surface sites, respectively. The sum $\sum^{(i)}$ runs over all NN sites of i. The mean magnetizations m_i vary with the index $n = 1, 2, \ldots$ labeling the lattice planes along the z axis, but are the same on each sublattice within a layer. Thus for the (110) surface, two variables are needed to describe the state of each layer:

$$m_i \equiv m_n^{\alpha}$$
 for $i \in \text{layer } n$, subl. α , $m_i \equiv m_n^{\beta}$ for $i \in \text{layer } n$, subl. β . (5)

The local order parameter ϕ_n is conveniently defined as

$$\phi_n \equiv \frac{1}{2} \left(m_n^{\alpha} - m_n^{\beta} \right) \,. \tag{6}$$

For the (100) surface, one may write

$$m_i \equiv m_n \quad \text{for } i \in \text{layer } n \,, \tag{7}$$

since each lattice plane belongs to a single sublattice. The definition of the local order parameter requires more care. The obvious choice $\phi_n \equiv \frac{1}{2}(-1)^{n+1}(m_n - m_{n+1})$ is physically reasonable but causes considerable problems in the continuum limit, as explained in detail in [3]. It is favorable to adopt the more symmetric definition

$$\phi_n \equiv \frac{1}{2} (-1)^{n+1} \left[m_n - \frac{1}{2} (m_{n+1} + m_{n-1}) \right] , \qquad (8)$$

which treats the preceding and succeeding layer on an equal footing.

The MF equations (4) have been studied in [3] both for (110) and (100) surfaces via the "nonlinear-mapping" technique [10]. It has been shown that in the case of the (100) surface a nonvanishing order parameter profile appears for $T > T_c$. The characteristic length scale that governs its exponential decay at large z diverges as $T \to T_c$. Precisely at $T = T_c$, the decay takes the form $z^{-\beta/\nu}$ (where $\beta = \nu = 1/2$ within MF theory), which is one of the signatures of the normal transition. In the case of the (110) surface, the local order parameter vanishes for $T > T_c$ since $m_n^{\alpha} = m_n^{\beta}$. Nevertheless one obtains a nontrivial magnetization profile, so that A rich and B rich layers alternate as one moves along the z direction. However, the length scale associated with this profile remains finite at $T = T_c$.

3 Continuum (Landau-Ginzburg) model

In proceeding to a suitable continuum description one must be aware of several novel features arising for Ising antiferromagnets or binary alloys, which are not present in simpler systems equivalent to the Ising ferromagnet. First, the Landau expansion of the surface free energy should look different for distinct orientations, due to the loss of the $\phi \to -\phi$ symmetry for symmetry-breaking surfaces (cf. Sec. 2.2). Second, one has to take into account so-called "non-ordering" (or noncritical) densities. In the alloy picture these are needed to account for spatially varying profiles of, e. g., the local concentration that could *not* be described by the order parameter alone.

Non-ordering densities introduce additional length scales that may compete with the order parameter correlation length ξ_b . It has been shown in a study of wetting in fcc Ising antiferromagnets that this competition may even lead to nonuniversal critical wetting exponents, and that the number of non-ordering densities depends on the orientation of the surface. Of course, noncritical densities do not affect the asymptotic surface critical behavior if the bulk transition is continuous (as in our case of a bcc antiferromagnet), since then the diverging correlation length ξ_b dominates all other length scales. However, we are interested here in phenomena $below T_c$, where ξ_b is finite. Accordingly, length scales associated with such spatially varying non-ordering densities may well be of the same order and important.

To become more specific, let us recall the Landau-Ginzburg model derived and critically examined in Ref. [3] for the case of the *symmetry-breaking* (100) surface. This is based on a free-energy functional of the form

$$\mathcal{F}\{\phi\} = \int_0^\infty dz \left\{ \frac{c}{2} \left(\frac{d\phi}{dz} \right)^2 + f_b \left[\phi(z) \right] \right\} + f_s(\phi_s) , \qquad (9)$$

where $\phi_s \equiv \phi(0)$. The Landau expansions of the bulk and surface free-energy densities read

$$f_b(\phi) = \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + \mathcal{O}(\phi^6), \quad f_s(\phi_s) = -g_1\phi_s + \frac{c}{\lambda}\phi_s^2 + \mathcal{O}(\phi_s^3).$$
 (10)

As expected, arbitrary odd powers of ϕ_s occur in the expansion of $f_s(\phi_s)$. In view of the above discussion it is remarkable that no spatially varying nonordering density appears in (9). The reason is that lattice planes belonging to sublattice α and β alternate along the [100] (or z) direction. Hence the order parameter profile uniquely determines the segregation profile and vice versa. By contrast, the nontrivial segregation profile present for the (110) surface above T_c provides a typical example of a spatially varying non-ordering density ψ appearing in the corresponding free-energy functional [11]. The "segregation field" H_1 then couples linearly to ψ , but no terms linear in the local order parameter and thus no ordering surface field are present.

Deriving the continuum theory from the lattice model has the virtue of relating the "phenomenological" coefficients in (10) explicitly to the "microscopic" parameters:

$$K \equiv \frac{4|J|}{k_B T} \; , \; h \equiv \frac{H}{4|J|} \; , \; h_1 \equiv \frac{H_1}{4|J|} \; ,$$
 (11)

which are dimensionless measures of the spin coupling strength and the bulk and surface magnetic fields. The "bulk" coefficients a, b, and c are independent of surface properties and depend on K and h only: a = a(K, h) etc. As usual, a varies linearly with the reduced temperature $t = (T - T_c)/T_c$ near T_c (at fixed magnetic field h), whereas b and c are positive constants to lowest order in t (see [3]). The "surface" parameters are found to be:

$$\lambda(K, h) = 1, \ g_1(K, h, h_1) = h_1 + m_{dis}(K, h),$$
 (12)

where $m_{\rm dis}=m_{\rm dis}(K,h)$ is the magnetization of the disordered state. The latter is thermodynamically stable only for $T>T_c$. The surface field h_1 enters only in the "effective" ordering field g_1 . The so-called extrapolation length λ (whose inverse $c_0\equiv 1/\lambda$ is conveniently called surface enhancement) is positive as it should be if the surface interactions are not enhanced.

In order to better understand the expression for g_1 it is helpful to recall some general symmetry properties of the Ising Hamiltonian (1) which should be respected by the continuum theory. If one replaces h and h_1 by its negative, the mean magnetizations and the local order parameter (6) behave as $m_i \to -m_i$, $\phi_n \to -\phi_n$, implying that the ordering surface field should change sign, too:

$$g_1(K, -h, -h_1) = -g_1(K, h, h_1).$$
 (13)

For bulk field h = 0 and arbitrary h_1 , the Ising antiferromagnet is exactly equivalent to an Ising ferromagnet since flipping all Ising spins on one sublattice and changing the sign of K leaves the partition function invariant. For the semi-infinite ferromagnet, however, an ordering field g_1 is merely equivalent to a surface magnetic field acting on the spins of the first layer and one easily finds [10]:

$$g_1(K, 0, h_1) = h_1. (14)$$

The expression (12) fulfills both (13) and (14). That the bulk magnetization m_{dis} of the disordered phase comes into play can be understood as follows. For $T > T_c$,

the order parameter profile should vanish identically if $g_1(K, h, h_1) = 0$. Hence the layer magnetization profile m_n must be a constant, $m_n \equiv m_{\text{dis}}(K, h)$. By Eq. (4), the molecular fields acting on surface and bulk spins are $H + H_1 - 4|J| m_2$ and $H - 4|J|(m_{n-1} - m_{n+1})$, respectively. Thus the flat profile is a solution if and only if $h_1 = -m_{\text{dis}}(K, h)$. Below T_c a thermodynamically unstable solution $m_n \equiv m_{\text{dis}}$ (i. e. $\phi_n \equiv 0$) still exists if and only if $h_1 = -m_{\text{dis}}(K, h)$. In order that this unstable solution survives the continuum approximation, one again has to demand that $g_1(K, h, h_1) = 0$ if $h_1 = -m_{\text{dis}}(K, h)$.

4 Wetting phase diagrams

The physical picture behind the wetting behavior at a (100) surface is the following. Below T_c , two ordered bulk phases $\pm \phi_b$ coexist. If, e. g., the effective ordering field g_1 is positive, the surface favors the phase $\phi_b > 0$, i. e. A atoms tend to occupy sublattice α planes $n = 1, 3, \ldots$ while B atoms reside preferentially on the β planes $n=2,4,\ldots$ However, it may occur that deeper in the bulk the role of the two sublattices is interchanged and the order parameter assumes the value $-\phi_b$ there. Then an antiphase domain boundary separating two regions of ordered phase appears. Antiphase boundaries always occur in real alloys below the ordering temperature. They are the analogs of domain walls. Now one may ask how the thickness of this "adsorbed" layer of bulk phase behaves when the temperature is varied. If the interface stays within a finite distance from the surface for $T < T_w$ while moving arbitrarily away into the bulk for $T > T_w$, a wetting transition takes place at $T_w = T_w(h_1, h)$. The thickness of the layer may either grow continuously as $T \uparrow T_w$ (second-order wetting transition), or jump from a finite value below T_w to infinity for $T \geq T_w$ in a first-order transition. Within standard wetting terminology we thus study complete wetting at coexistence [7].

We have calculated the wetting phase diagram in the space of physical param-

eters $t = (T - T_c)/T_c$ (reduced temperature), h, and h_1 . To this end we employed the full expressions for the bulk and surface Landau free energies f_b and f_s in (9) to be found in [3], and used the standard equal-area construction to locate the transitions [12]. Of course, a description in terms of continuum mean-field theory is only sensible above the roughening temperature T_R [13], where $T_R \simeq \frac{1}{3}T_c$ for h = 1 [9]. For $T < T_R$ the growth of the wetting layer proceeds via an infinite sequence of layering transitions which are outside the scope of the continuum theory. Fig. 2 shows two representative phase diagrams at fixed bulk fields h=1and h = 1.5. The tricritical point separating continuous and first-order transition lines on the right branch of the phase diagram (where $g_1 > 0$) is found to depend strongly on the bulk field for h larger than ≈ 1.5 . Critical wetting then occurs over a wide temperature range. (If |h| > 2, the ordered phases are energetically unstable at T=0 and the bulk phase transition ceases to exist.) In order to interpret Fig. 2 an exact groundstate analysis may be carried out similar to the one in [13], from which one easily finds that complete wetting already occurs at T=0 if $|h_1| \geq 1$. Thus continuum mean-field theory certainly fails if wetting transitions at finite temperatures are predicted for $|h_1| > 1$. In this case one has to resort to the discrete mean-field theory for a more accurate description of the low-temperature part of the phase diagram.

Acknowledgments

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Figure captions

Fig. 1. Disordered (A2) and ordered (B2) structures of a bcc binary (AB) alloy. Black and white circles denote A and B atoms (or sublattice α and β sites), respectively. The hatched planes represent the (100) and (110) surface orientations.

Fig. 2. Wetting phase diagrams at fixed bulk fields h = 1 and h = 1.5, exhibiting continuous (full lines) and first-order wetting transitions (dashed lines), where $t = (T - T_c)/T_c$ denotes the reduced temperature. One has $g_1 > 0$ ($g_1 < 0$) to the right (left) of the dashed-dotted lines where $g_1 = 0$.



